(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 February 2002 (14.02.2002)

PCT

(10) International Publication Number
WO 02/12356 A2

(51) International Patent Classification[7]: C08F 8/00

(21) International Application Number: PCT/US01/25283

(22) International Filing Date: 10 August 2001 (10.08.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/224,126 10 August 2000 (10.08.2000) US

(71) Applicant *(for all designated States except US)*: **E.I. DUPONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) **Inventor; and**
(75) **Inventor/Applicant** *(for US only)*: **HOFMANN, George, Henry** [US/US]; 102 Weldin Park Drive, Wilmington, DE 19803 (US).

(74) **Agent: DOBSON, Kevin, S.**; E.I. Dupont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).

(81) **Designated States** *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) **Designated States** *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/12356 A2

(54) **Title:** PROCESS FOR CONVERSION OF POLYVINYL BUTYRAL (PVB) SCRAP INTO PROCESSABLE PELLETS

(57) **Abstract:** The present invention relates to a polyvinylbutyral (PVB) composition that is useful for blending with other polymers. The PVB composition of the present invention can be stored and used at ambient temperature without the occurrence of blocking by the PVB.

TITLE

PROCESS FOR CONVERSION OF POLYVINYL BUTYRAL (PVB) SCRAP INTO PROCESSABLE PELLETS

This application claims the benefit of U.S. Provisional Application No. 60/224,126, filed August 10, 2000.

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a process for preparing pellets from polyvinyl butyral scrap material. This invention particularly relates to a process for preparing pellets of modified polyvinyl butyral useful for preparing blended polyvinyl butyral compositions.

Description of the Related Art

Polyvinyl butyral (PVB) is a thermoplastic material useful for imparting shatter-resistance to glass in such applications as windshields for automobiles and window glass in homes and buildings, for example. The preparation of polyvinyl butyral is known, and is practiced commercially. For example, Butacite® is a polyvinyl butyral product manufactured by DuPont. Solutia also manufactures polyvinyl butyral products.

PVB scrap can be generated during a PVB manufacturing process, for example, if process errors occur that result in off-quality production rolls or otherwise unusable material. In preparing windshields and other laminate articles comprising a polyvinyl butyral layer, glass manufacturers can generate PVB scrape material when trimming excess PVB from the edges of a glass laminate, or from production errors resulting in unusable products. Conventional practice is to incinerate PVB scrap material at a cost to the manufacturer. This can be an expensive practice because millions of pounds of PVB scrap material are incinerated each year.

It is known that PVB blends with other polymer materials have utility. For example, U.S. Patent No. 5,514,752 describes PVB/polypropylene blends, and U.S. Patent No. 5,770,654 describes

PVB/polyamide blends. PVB can improve the flexibility, polarity and toughness of polyolefins, polyamides, and polyvinylchloride. However, use of PVB in polymer blends is not without problems.

PVB is a material that can be difficult to work with because of the tendency of PVB to adhere to itself. Sheets of PVB can stick together, or bind, with such strength that it is very difficult to separate the layers - even to the extent that the layers cannot be separated. Such irreversible self-adhesion by PVB is referred to in the art of PVB manufacture as "blocking". Once PVB "blocks", it can be extremely difficult, if not impossible, to process. PVB is generally stored cold to reduce the tendency to block. Refrigerated vehicles are used to ship PVB for the same reason. The tendency to block can make manufacturing processes that incorporate PVB very complex and difficult. Continuous processes that in which PVB is handled can be very expensive processes to run, and therefore are not practical commercial operations. Blends of PVB with other materials can block in the same manner as homogenous PVB compositions. Therefore, blends of PVB with other polymers can be difficult to obtain in a cost effective manner.

It is an object of the present invention to reduce the amount of polyvinylbutyral scrap that is sent for incineration. It is a also an object of the present invention to convert polyvinylbutyral scrap material into a processable form. It is further an object of the present invention to convert polyvinylbutyral scrap material into pellets, useful for preparing PVB/polymer blends. It is still a further object of the present invention to convert polyvinylbutyral scrap material into commercially useful polymer blends.

SUMMARY OF THE INVENTION

The present invention is a non-blocking chemically modified polyvinylbutyral (PVB) composition comprising a chemically modified PVB, wherein the modified PVB is the reaction product of unmodified polyvinylbutyral, having hydroxyl functionality, and a second component

or mixture, wherein the second component reacts with at least a portion of the hydroxyl functionality of the PVB.

In another aspect, the present invention is a process for converting polyvinylbutyral (PVB) into pellet form, wherein the pellets do not become irreversibly joined, the process comprising the steps: obtaining a modified PVB composition by mixing PVB and a second component under conditions suitable to cause a reaction between PVB and the second component, wherein the second component can chemically react with hydroxyl functionality present in a PVB polymer; converting the modified PVB composition into pellet form by physical or mechanical means at a temperature of greater than at least 20°C.

DETAILED DESCRIPTION OF THE INVENTION

In one embodiment, the present invention is a modified non-blocking polyvinylbutyral (PVB) composition. Unmodified PVB is an uncrosslinked gum that flows and masses together, that is it blocks, typically at temperatures above about 4°C (approximately 40°F). For this reason it is difficult to convert PVB into a blended material, particularly by a continuous process. Modified PVB of the present invention is free-flowing, without blocking (non-blocking) at temperatures above about 4°C, preferably at temperatures above about 20°C, more preferably at temperatures above about 50°C, and most preferably temperatures above about 60°C, and can be useful in a continuous compounding operation to obtain other PVB blends.

In the present invention, the term "non-blocking materials" can include materials that can adhere to similar or identical compositions, but the adhesion can be overcome with varying degrees of force. For the purposes of the present invention, a composition can: (a) be completely non-adhesive, i.e. showing no tendency to self-adhere; (b) show slight, medium, or strong adhesion wherein polymeric pieces can be separated from one another but only with some degree of force; or (c) show irreversible adhesion wherein the polymer pieces cannot be separated even

with force. Non-blocking compositions of the present invention, include only compositions of types (a) and/or (b), hereinabove.

Without being bound by theory, non-blocking PVB compositions of the present invention have some measure of crystallinity. Modification of PVB can be by physical blending or by chemical modification. It is preferred for the purposes of the present invention that PVB be chemically modified to add crystallinity by covalently bonding to a second component. Modification of PVB in this manner can result in physical compatibility in blends of PVB with a second component. PVB has hydroxyl functionality, and can react with chemical compositions having functionality capable of reacting with hydroxyl groups. Chemical modification can occur when the PVB resin is reacted with a second component. The second component can be any polymer that is capable of reacting with the hydroxyl functionality of the PVB. For example, the second component can include carboxylic acid functionality or derivatives thereof. Such derivatives can include ester, anhydride, isocyanate, or acid chloride functionality, for example. Multicomponent mixtures of various hydroxyl-reactive functionalities can be useful in the practice of the present invention.

The second component can be monomeric, polymeric, or a mixed composition. Preferably the second component is a polymer composition that includes anhydride functionality, such as is available commercially from E. I. DuPont de Nemours and Company under the Fusabond® brand name, or carboxylic acid functionality. Fusabond® polymers are polyolefins having anhydride functionality.

In another embodiment, the present invention is a process for obtaining a pelletized, non-blocking PVB composition, the composition being useful in a continuous compounding operation, such as one wherein the modified PVB can be continuously compounded with other polymeric materials. The process comprises the step: mixing polyvinylbutyral with a second component under conditions wherein a chemical reaction will occur between the unmodified PVB and the second component. Such

conditions conducive for carrying out a chemical reaction can comprise the steps: (1) exposing the PVB and second component or mixture to a temperature such that a melt blend (melt) is obtained; (2) cooling the melt to obtain a solid composition of chemically modified PVB; and (3) pelletizing the solid composition. The PVB and second component can be mixed in a ratio of from about 1:100 to about 100:1 PVB:second component (parts per hundred parts, by weight). Preferably, the PVB and second component are mixed at a ratio of from about 5:1 to about 100:1, more preferably at a ratio of from about 10:1 to about 50:1, and most preferably from about 10:1 to about 25:1.

A melt blend of the preceding paragraph can be obtained by heating the PVB mixture at a temperature of from about 100°C to about 260°C. Preferably, the blend is obtained at a temperature of from about 120°C to about 255°. Most preferably, the melt blend is obtained at a temperature of from about 150°C to about 250°C.

An antioxidant is not required, however one is preferred. If included, the antioxidant can be present in an amount of at least about 0.1% by weight.

A modified-PVB composition of the present invention is non-blocking above a temperature of about 20°C. Particularly, a modified PVB composition is non-blocking above a temperature of about 50°C, more particularly above a temperature of about 60°C, and even more particularly above 75°C.

In another embodiment, the present invention is a process for preparing a blend of modified PVB with at least one other non-reactive polymer. For example, modified PVB can be blended with polypropylene, polyvinylchoride, nylon, olefinic copolymers such as acid copolymers, other thermoplastic materials, or mixtures thereof. PVB blends of the present invention can include a compatibilizer, which can make the modified PVB compatible with other components of the blend. The compatibilizer can be Fusabond®, for example. Blends of modified PVB can be obtained by either a batch process or a continuous process.

Polymer blends of modified PVB can be obtained in a continuous process by extrusion of pellets of modified PVB with, for example, polypropylene. Alternatively, blends of the present invention can be obtained by a batch process, using a mixer.

Modified PVB can be extruded in either a single screw extruder or a twin screw extruder, at temperatures in the range of from about 75°C to about 250°C. Modified PVB pellets can be obtained from extruded modified PVB, and can be blended with other thermoplastic polymers or copolymers by any means known in the art of preparing polymer blends. For example, blends can be obtained by extrusion, grinding, melt-blending, crushing, or other means of physically blending polymers.

Objects or articles comprising polymers of the present invention can be prepared from the polymers and polymer blends of the present invention by methods know to those skilled in the art.

EXAMPLES

The Examples are presented for illustrative purposes only, and not intended to limit the scope of the present invention in any way. PVB used in the Examples was recycled from windshield edge trim.

Examples 1-4

Four samples (A,B,C and D) of PVB/Fusabond mixture were prepared according to the following procedure, using the amounts shown in Table 1, below.

PVB, Fusabond® A MG-423D (ethylene/alkyl acrylate/CO copolymer that has been modified with 1% maleic anhydride graft) or Fusabond® P MD353D (polypropylene with 1.4% maleic anhydride graft), and Irgonox® 1010 were mixed at 230°C in a laboratory batch mixer until a homogeneous melt blend was obtained. The melt was removed and cooled quickly in dry ice. The mixture was dried in a vacuum oven at ambient temperature. The M.I. was determined at 190°C of 2160 grams. Shore A/D Hardness values were determined at 0 and 15 seconds.

Table 1

Sample[1]	Melt Index	Shore Hardness (0 sec /15 sec) A	D	Component (pph) PVB	F[a]	Irganox 1010
A (Ex.)	1.9	82/70	56/24	100.0	5.0	1.0
B (Ex.)	0.7	84/74	56/26	100.0	10	1.0
C (Ex.)	2.0	81/69	56/23	100.0	5.0	1.0
D (Ex.)	0.3	84/74	56/25	100.0	10.0	1.0
Control[@]	3.1	72/56	51/16	100.0	0	0

[a]Fusabond®. Samples A and B include Fusabond® A MG-423D; Samples C and D include Fusabond® P MD-353D.
[@]Not an example of the present invention. Typical values.

Examples 5-9

Blocking Test

1/16"x3"x6" plaques of each Sample were pressed at 190°C as was a PVB control. The plaques were cut in half (to make 3x3 squares) and one half placed on top of the other and put on a metal tray lined with Teflon coated aluminum foil. A 1"x3" 45-gram weight was placed on the layers and a thin strip of fep film was placed underneath the weight to prevent sticking of the weight to the samples. The Samples were exposed to relative humidity of 50% at 23° overnight. The following results were obtained.

Sample A (Ex. 5) exhibited slight sticking but was easily separated.

Sample B (Ex. 6) performed the same as A.

Sample C (Ex. 7) stuck slightly more than A, B, or D but was easily separated.

Sample D (Ex. 8) gave the same result as Samples A and B.

PVB control (Ex. 9) (100% PVB) could only be separated at the corners.

Examples 10 - 14

Samples A, B, C, D, and a PVB control were prepared as above and then exposed to 38°C temperature in an air circulating oven on a metal tray lined with Teflon® coated foil for 24 hours. The Samples were allowed to cool on metal tray, with weight in place, for a period of 30 minutes. The following results were obtained.

Samples A (Ex. 10), B (Ex. 11), and C (Ex. 12) - the layers stuck together where the weight was in place.
Sample D (Ex. 13) - the layers separated cleanly, but with some resistance.
PVB control (Ex. 14) - the layers completely self-adhered (blocked).

Example 15

Sample D was put through the above conditions except that the temperature was raised to 44°. The same result was obtained as above for Sample D.

Example 16 – 35

Samples G through K2 were prepared having the compositions shown in Table 2. The Samples were prepared using a Haake laboratory batch mixer. PVB, polypropylene (Profax®) or high density polyethylene, and Fusabond with Irgonox 1010 were mixed at 200°C until a homogeneous melt blend was obtained. The melt was removed and cooled quickly in dry ice. The mixture was dried in a vacuum oven at ambient temperature. The Control is unblended, unmodified PVB sheet from recycled edge trim. The melt index was measured at 190°C, 2160 grams, and reported for each in Table 2. Shore A and D for each is reported in Table 2. Adhesion was tested as described hereinabove and the results are reported in Table 3.

Table 2

		Shore Hardness (0 sec /15 sec)		Component (pph)		
Sample[1]	Melt Index	A	D	PVB	F[a]	PP[b]
G (Ex. 16)	4.4	73/59	47/19	100	2.5	7.5
H (Ex. 17)	2.9	63/52	46/18	100	5.0	5.0
I (Ex. 18)	3.1	66/53	46/18	100	7.5	2.5
J (Ex. 19)	1.7	75/61	49/19	100	10	0.0
K (Ex. 20)	4.5	80/69	54/24	100	5.0	10.0
K2 (Ex. 20)	3.1	81/68	49/22	100	5.0	10.0[x]
Control[@]	3.1	72/56	51/16	100	0	0

[1]All samples include 0.1 pph Irganox® 1010 antioxidant, except for the Control, which has no antioxidant.
[@]Not an example of the present invention. Typical values.
[a]F = Fusabond®, all samples except for K2 include Fusabond® P MD 353D; K2 includes Fusabond® E MB496D which is high density polyethylene/1.2% maleic anhydride graft.
[b]PP is polypropylene (Profax® 6323) which is polypropylene of melt index 5.0.
[x]K2 includes high density polyethylene, melt index 14, instead of polypropylene.

Table 3

Sample	Adhesion after treatment @ Temperature (°C)			Separation after treatment @ Temperature (°C)		
	23	38	44	23	38	44
E (Ex. 21)	sl	st	--	easily	x	--
F (Ex. 22)	sl	m	m	easily	yes	yes
G (Ex. 23)	sl	sl	sl	easily	easily	easily
H (Ex. 24)	sl	sl	sl	easily	easily	easily
I (Ex. 25)	sl	sl	sl	easily	easily	easily
J (Ex. 26)	sl	sl	sl	easily	easily	easily
K (Ex. 27)	none	none	none	easily	easily	easily
K2 (Ex. 28)	none	sl	sl	easily	easily	easily
Control[@]	st	--	--	x	--	--

[@]Not an example of the present invention.
none = no adhesion; sl = slight adhesion; m = medium adhesion; st = strong adhesion
easily = easily separated; yes = separated with effort; x = did not separate

Examples 36 – 44

Samples L through T were prepared having the compositions shown in Table 4. The Samples were prepared using a Haake laboratory batch mixer. PVB, Elvaloy® 441 (ethylene/n-butyl acrylate/CO terpolymer available from E.I. DuPont de Nemours and Company) with an MI of 10 or Elvaloy® 741 (ethylene/vinyl acetate/CO terpolymer available from E.I. DuPont de Nemours and Company) with a MI of 35, and Fusabond® A with Irgonox® 1010 were mixed at 200°C until a homogeneous melt blend was obtained. The melt was removed and cooled quickly in dry ice. The mixture was dried in a vacuum oven at ambient temperature. The Control is unblended, unmodified PVB sheet from

recycled edge trim. The melt index was measured at 190°C, 2160 grams, and reported for each in Table 4. Shore A and D for each is reported in Table 4. Adhesion was tested as described hereinabove and the results are reported in Table 5.

Table 4

		Shore Hardness (0 sec/15 sec)		Component (pph)			
Sample	Melt Index	A	D	PVB	Fusabond® A MG-423D	Elvaloy® 441	Irganox® 1010
N (Ex. 31)	2.7	76/60	48/17	100	2.5	7.5	0.1
O (Ex. 32)	3.5	79/61	53/17	100	5.0	5.0	0.1
P (Ex. 33)	2.9	75/58	51/18	100	7.5	2.5	0.1
Q (Ex. 34)	3.1	79/63	55/17	100	10	0.0	0.1
R (Ex. 35)	1.8	80/71	54/24	100	5.0	10.0	0.1
S (Ex. 36)	2.2	80/67	49/22	100	5.0	5.0*	0.1
T (Ex. 37)	1.1	86/72	55/25	100	5.0	10*	0.1
Control@	3.1	72/56	51/16	100	0	0	0

@Not an example of the present invention. Typical values.

Table 5

	Adhesion after treatment @ Temperature (°C)			Separation after treatment @ Temperature (°C)		
Sample	23	38	44	23	38	44
N	sl	sl	sl	easily	easily	easily
O	sl	sl	m	easily	easily	yes
P	sl	m	m	easily	yes	yes
Q	sl	st	st	easily	yes+	yes+
R	none	none	none	easily	easily	easily
S	none	m	m	easily	yes	yes
T	none	none	none	easily	easily	easily
Control@	st	--	--	x	--	--

@Not an example of the present invention.
none = no adhesion; sl = slight adhesion; m = medium adhesion; st = strong adhesion
easily = easily separated; yes = separated with slight effort; yes+ = separated with force; x = did not separate

Examples 45 – 47

2000 pounds each of pellet Samples (U – V) were obtained on a Banbury mixer operated at 177°C (350°F) coupled with a single screw pelletizing extruder from the compositions shown in Table 6. Adhesion was tested as described hereinabove and none of the samples showed any self-adhesion.

Table 6

			Component (pph)					
Sample	Melt Index	Shore A Hardness (init./15 sec)	PVB	F-P[1]	F-A[2]	Elvaloy® 441	Profax® 6323[4]	Irganox® 1010
U[3]	5.2	75/63	100	5.0	0.0	0.0	10	0.1
V[3]	3.6	78/66	100	5.0	0.0	0.0	5.0	0.1
W[3]	1.4	84/74	100	0.0	5.0	10	0.0	0.1

[1]Fusabond® P MD-353D
[2]Fusabond® A MG-423D
[3] No adhesion observed.
[4]MI = 5

Examples 48, 50, and 52

In these examples, Sample U was pellet-blended with polypropylene in the proportions indicated in Table 7, and fed as a single stream into a 30 mm twin-screw extruder. Samples U3 and U4 included calcium carbonate filler. Physical properties were tested and the results recorded in Table 7 and 8.

Examples 49, 51, and 53

In these examples, Sample V was pellet-blended with polypropylene in the proportions indicated in Table 7, and fed as a single stream into a 30 mm twin-screw extruder. Samples V3 and V4 included calcium carbonate filler. Physical properties were tested and the results recorded in Tables 7 and 8.

Table 7

	MI @ 190°C		Shore Hardness (0 sec /15 sec)		Component (pph)				
Sample	@ 2160 g	@ 21.6 kg	A	D	Sample U	Sample V	PX 6823	IRG	$CaCO_3$
U2	2.7	256	83/74	56/28	690	0	30	1.0	0
U3	1.9	188	88/82	63/34	690	0	30	1.0	200
U4	1.2	133	87/83	64/39	690	0	30	1.0	400
V2	1.7	152	85/78	59/29	0	660	60	1.0	0
V3	1.4	120	89/84	64/37	0	660	60	1.0	200
V4	0.9	97	90/86	63/38	0	660	60	1.0	400

PX 6823 is Profax® 6823 (polypropylene of MI = 0.2).

Table 8

Sample	Initial Modulus (psi)	Tensile Strength @ Max (psi)	Elongation @ Max (%)	Tensile Strength @ Break (psi)	Elongation @ Break (%)
U2	1412	4518	287	4513	288
U3*	2255 (1495)	2569 (3218)	162 (234)	2501 (3216)	164 (234)
U4*	4308 (2557)	1894 (2308)	65 (154)	1624 (2292)	69 (157)
V2	2446	4281	284	4275	284
V3	3544	2744	152	2733	155
V4	3553	2412	132	2369	135

*Samples appeared undermixed and were re-extruded to give the values shown in parentheses.

Examples 54 – 56

Samples X through Z were prepared having the compositions shown in Table 9. The Samples were prepared using a Haake mixer. PVB, polypropylene (Profax®), and Fusabond P with Irgonox 1010 were mixed at 200°C until a homogeneous melt blend was obtained. The melt was removed and cooled quickly in dry ice. Samples X and Z included calcium carbonate filler. The mixtures were dried in a vacuum oven at ambient temperature. Physical properties were tested and the results recorded in Tables 9 and 10.

Table 9

	MI @ 190°C		Shore Hardness (0 sec/15 sec)		Component (pph)				
Sample	@ 2160 g	@ 21.6 kg	A	D	PVB	F-P	PX 6723	IRG	$CaCO_3$
X	2.6	238	82/73	48/26	600	20	100	1.0	0
Y	2.1	216	79/70	58/32	600	20	100	1.0	200
Z	1.5	179	91/88	70/42	600	20	100	1.0	400

PX 6723 is Profax® 6723 (polypropylene of MI = 0.3.

Table 10

Sample	Initial/Flex Modulus (psi)	Tensile Strength @ Max (psi)	Elongation @ Max (%)	Tensile Strength @ Break (psi)	Elongation @ Break (%)
X	1404/1048	3584	279	3580	279
Y	1577/1341	3019	242	2992	242
Z	2678/2749	2479	203	2477	203

Examples 57 – 64

Samples NY1 – NY4 and NU1 – NU 4 were prepared having the compositions shown in Table 11. The Samples were prepared using a Haake mixer. For Nylon blends, PVB, Nylon 6, and Irgonox 1010 were mixed at 230°C until a homogeneous melt blend was obtained. For Nucrel® blends PVB, Nucrel® and Irganox 1010 were mixed at 210°C. Each melt was removed and

cooled quickly in dry ice. The mixtures were dried in a vacuum oven at ambient temperature. The Control is unblended, unmodified PVB sheet from recycled edge trim. The melt index of each sample was measured at 190°C, 2160 grams, and reported for each in Table 11. Shore A and D for each is reported in Table 11. Adhesion was tested as described hereinabove and the results are reported in Table 12.

Examples 57A – 57E

Samples NY5 – NY9 were prepared having the compositions shown in Table 11A. The Samples were prepared using a Haake mixer. PVB, Nylon 6, amorphous nylon (Selar 3426) and Irgonox 1010 were mixed at 230°C until a homogeneous melt blend was obtained. Nylon 6 was added for additional crystallinity. Each melt was removed and cooled quickly in dry ice. The mixtures were dried in a vacuum oven at ambient temperature. The Control is unblended, unmodified PVB sheet from recycled edge trim. The melt index of each sample was measured at 190°C, 2160 grams, and reported for each in Table 11A. Shore A and D for each is reported in Table 11A. Adhesion was tested as described hereinabove and the results are reported in Table 12A.

Table 11

		Shore Hardness (0 sec/15 sec)		Component (pph)			
Sample	Melt Index	A	D	PVB	Capron® 8202	Nucrel® 0407[a]	Irganox® 1010
NY1	3.9	67/52	48/16	100	5.0	0	0.1
NY2	3.1	68/56	46/19	100	10	0	0.1
NY3	2.1	71/61	53/23	100	20	0	0.1
NY4	1.0	76/70	58/30	100	40	0	0.1
NU1	4.8	68/53	46/15	100	0	5.0	0.1
NU2	4.1	68/55	48/17	100	0	10	0.1
NU3	4.8	75/62	47/18	100	0	20	0.1
NU4	8.6	76/67	45/21	100	0	40	0.1
Control[@]	3.1	72/56	51/16	100	0	0	0

[@]Not an example of the present invention. Typical values.
[a] 4% methacrylic acid. MI = 7.

Table 11A

		Shore Hardness (0 sec/15 sec)		Component (pph)			
Sample	Melt Index	A	D	PVB	Nylon 6 (Capron 8202)	Selar 3426[a]	Irganox® 1010
NY5	3.9	73/61	49/20	100	5.0	5.0	0.2
NY6	2.7	69/61	48/23	100	10	5.0	0.2
NY7	2.5	76/65	51/24	100	15	5.0	0.2
NY8	3.1	74/63	51/23	100	5.0	10	0.2
NY9	3.5	79/71	56/25	100	10	10	0.2
Control[@]	3.1	72/56	51/16	100	0	0	0

[@]Not an example of the present invention.

[a] Amorphous nylon having carboxylic acid functionality.

Table 12

	Adhesion after treatment @ Temperature (°C)			Separation after treatment @ Temperature (°C)		
Sample	23	38	44	23	38	44
NY1	m	m	st	yes	yes	x
NY2	m	m	st	yes	yes	yes+
NY3	sl	m	st	easily	yes	yes+
NY4	none	m	st	easily	yes	yes+
NU1	sl	st	st	easily	yes+	yes+
NU2	sl	m	st	easily	yes	yes+
NU3	sl	sl	sl	easily	easily	easily
NU4	none	none	none	easily	easily	easily
Control[@]	st	--	--	x	--	--

[@]Not an example of the present invention.

none = no adhesion; sl = slight adhesion; m = medium adhesion; st = strong adhesion

easily = easily separated; yes = separated with slight effort; yes+ = separated with force; x = did not separate

Table 12A

	Adhesion after treatment @ Temperature (°C)			Separation after treatment @ Temperature (°C)		
Sample	23	38	44	23	38	44
NY5	sl	m	m	easily	yes	yes
NY6	sl	sl	m	easily	easily	yes
NY7	sl	sl	sl	easily	easily	easily
NY8	m	m	m	yes	yes	yes
NY9	sl	m	st	easily	yes	yes+
Control[@]	st	--	--	x	--	--

[@]Not an example of the present invention.

none = no adhesion; sl = slight adhesion; m = medium adhesion; st = strong adhesion

easily = easily separated; yes = separated with slight effort; yes+ = separated with force; x = did not separate

Examples 65 – 74

Samples PPG1 through PPG8 were prepared having the compositions shown in Table 13. The Samples were prepared using a 30 mm twin screw extruder. PVB pellets (Modifier G), polypropylene (Profax®) and Fusabond®

pellet blend were extrusion compounded at 230°C. The melt was quenched in water and pelletized. Samples PPG7 and PPG8 included calcium carbonate as filler. The pellets were dried in a vacuum oven at ambient temperature. Physical properties were tested and the results recorded in Tables 13 and 14. Samples PPG9 and PPG10 were obtained by re-mixing samples PPG1 and PPG2, respectively, with an additional 10 parts of Fusabond® in the batch mixer.

Table 13

	MI @ 190°C			Component (pph)			
Sample	@ 2160 g	@ 21.6 kg	Shore D Hardness (0 sec /15 sec)	Modifier G[a]	F-P[b]	PP[c]	$CaCO_3$
PPG1	0.8	103	76/57	70	0	100	0
PPG2	1.2	167	70/52	120	0	100	0
PPG3	0.6	89	63/42	220	0	100	0
PPG4	0.1	26	65/46	220	10	100	0
PPG5	1.4	160	55/33	420	0	100	0
PPG6	2.3	190	54/31	620	0	100	0
PPG7	1.6	184	60/38	620	0	100	200
PPG8	1.0	129	64/42	620	0	100	400
PPG9	0.3	40	74/56	70	10	100	0
PPG10	0.3	58	70/52	120	10	100	0

[a]Modifier G is Sample U, hereinabove.
[b]F-P is Fusabond® P.
[c]PP is polypropylene Profax® 6823, M.I. = 0.2.

Table 14

Sample	Internal Modulus (psi)	Tensile Strength @ Max (psi)	Elongation @ Max (%)	Tensile Strength @ Break (psi)	Elongation @ Break (%)
PPG1	49639	3548	24	3240	185
PPG2	37440	3718	187	3088	200
PPG3	13297	5049	284	5041	284
PPG4	26476	5188	278	5183	278
PPG5	2568	4651	296	4644	296
PPG6	2106	4276	268	4272	268
PPG7	4246	2203	111	2195	115
PPG8	5400	2319	110	2315	113
PPG9	50790	4443	229	4428	232
PPG10	39080	3922	181	3915	177

Examples 75 – 78

Samples MG1, MG2, ME1, and ME2 were prepared having the compositions shown in Table 15. The Samples were prepared using a Haake mixer. PVB pellets, polypropylene (Profax®), and Fusabond® (with Irgonox 1010) were mixed at 200°C until a homogeneous melt blend was obtained. The melt was removed and cooled quickly in dry ice. Samples MG2 and ME2

included calcium carbonate filler. The mixtures were dried in a vacuum oven at ambient temperature. Physical properties were tested and the results recorded in Tables 15 and 16.

Table 15

		Shore Hardness (0 sec /15 sec)		Component (pph)				
Sample	MI @ 190°C @ 2160 g	A	D	Sample K	Sample K2	PP[1]	IRG	$CaCO_3$
MG1	4.9	74/65	55/24	690	0	30	1.0	0
ME1	4.0	80/71	50/25	0	690	30	1.0	0
MG2	5.1	86/80	61/35	690	0	30	1.0	400
ME2	4.4	87/79	58/35	0	690	30	1.0	400

[1]PP is polypropylene Profax® 6823, M.I. = 0.2.

Table 16

Sample	Internal Modulus (psi)	Tensile Strength @ Max (psi)	Elongation @ Max (%)	Tensile Strength @ Break (psi)	Elongation @ Break (%)
MG1	792	3126	287	3120	287
ME1	672	3131	282	3123	282
MG2	1493	1685	139	1628	146
ME2	1562	1727	167	1714	169

Examples 79 – 85

Samples PVC1 through PVC7 were prepared having the compositions shown in Table 17. The Samples were prepared using a Haake batch mixer. Modifier H (Sample W above), polyvinylchloride, and, optionally, Fusabond® were mixed at 200°C until a homogeneous melt blend was obtained. The melt was removed and cooled quickly in dry ice. Sample PVC7 included calcium carbonate. The blends were dried in a vacuum oven at ambient temperature. Physical properties were tested and the results recorded in Tables 17 and 18.

Table 17

	MI @ 190°C @ 21.6 kg		Component (pph)			
Sample		Shore D Hardness (0 sec /15 sec)	Modifier H[a]	F-A[b]	PVC[c]	$CaCO_3$
PVC1	10	74/62	58	0	100	0
PVC2	13	75/60	58	2.5	100	0
PVC3	10	75/61	58	5	100	0
PVC4	26	63/42	220	0	100	0
PVC5	31	57/35	420	0	100	0
PVC6	28	55/31	620	0	100	0
PVC7	13	60/38	620	0	100	400

[a]Modifier H is Sample W, hereinabove.
[b]F-A is Fusabond® A.
[c]PVC is polyvinylchloride (100 parts Vista 5305, 4 parts Mark 1900, 1part Seenox 4125, 1 part 1098 stabilizers and 3 parts wax E lubricant)

Table 18

Sample	Tensile Strength @ Max (psi)	Elongation @ Max (%)	Tensile Strength @ Break (psi)	Elongation @ Break (%)
PVC1	4377	152	4139	154
PVC2	4902	185	4598	188
PVC3	4510	188	4509	188
PVC4	4096	239	4090	238
PVC5	3990	251	3982	251
PVC6	4005	268	3996	268
PVC7	2489	209	2486	209

Examples 79A – 79D

Pellets of Modifier H and PVC powder were continuously fed to a 30 mm Buss Kneader and melt compounded at 200°C, strand quenched and pelletized in a continuous manner. Physical properties of injection molded parts were measured and recorded in Table 17A and 18A.

Table 17A

Sample	MI @ 190°C @ 21.6 kg (@ 2.16 kg)	Shore D Hardness (0 sec /15 sec)	Component (pph)		
			Modifier H[a]	PVC[*]	Atomite Whiting
PVC8	23 (0.2)	65/42	220	105	0
PVC9	18 (0.1)	56/32	420	105	0
PVC10	50 (0.5)	55/32	620	105	0
PVC11	45 (0.4)	62/40	620	105	400

[a]Modifier H is Sample W, hereinabove.
[*]PVC is polyvinylchloride (100 parts Vista 5305, 4 parts Mark 1900, 1part Seenox 4125, 1 part 1098 stabilizers and 3 parts wax E lubricant)

Table 18A

Sample	Tensile Strength @ Max/Break/Yield (psi)	Elongation @ Max/Break/Yield (%)	Flexural Modulus (psi)	Not. Izod (ft-lbs/in)	Gardner Impact[1] (in.-lbs.) @ 23°C (-30°C)
PVC8	2827/2751/727	180/188/8	17077	NB	NB (24)
PVC9	2682/2044/535	213/249/9	8262	NB	NB (30)
PVC10	2641/2446/309	270/283/9	3096	NB	NB (22)
PVC11	1817/1721/412	134/183/7	7272	NB	NB (16)

[1]1/8" plaques, NB IS>320.

Examples 86 - 91

In these examples, the components were continuously fed into a 30 mm twin-screw extruder and melt compounded at 240°C, quenched and pelletized in a

continuous process. Physical properties were tested on injection molded parts and the results recorded in Tables 19 and 20.

Table 19

Sample[1]	Component (pph)		Not. Izod (ft-lbs./in)		MI @ 230°C @ 2160 g	Shore D Hardness (0 sec /15 sec)
	Modifier G[a]	Ny[b]				
NYG1	0	100	1.2[c]	1.1[d]	29	84/73
NYG2	5	95	1.7[c]	1.7[d]	27	83/72
NYG3	10	90	1.3[c]	1.8[d]	24	80/70
NYG4	20	80	1.9[c]	2.4[d]	20	77/68
NYG5	30	70	2.6[c]	2.8[d]	15	78/66
NYG6	40	60	3.1[c]	3.7[d]	16	77/65

[1]Samples include 0.1 pph Irganox® 1010
[a]Modifier G is Sample U, hereinabove.
[b]Nylon 6 (Capron 8202).
[c]Gate.
[d]Far.

Table 20

Sample	Tensile Strength @ Max/Break/Yield (psi)	Elongation @ Max/Break/Yield (%)	Flexural Modulus (psi)	Gardner Impact[1] (in.-lbs.) @ 23°C (-30°C)
NYG1	9097/5692/9069	11/119/11	175929	256 (124)
NYG2	8121/6155/8110	10/185/11	158759	280 (160)
NYG3	9002/8901/7370	291/299/11	157952	NB[*] (152)
NYG4	7830/7783/5804	270/272/16	136746	NB (144)
NYG5	7164/7059/5021	248/249/33	119748	NB (148)
NYG6	6740/6734/4634	256/257/41	83800	NB (168)

[1]1/8" plaques, NB IS>320.
[*]NB is "no break".

Examples 92 - 97

In these examples, the pellet components were continuously fed into a 30 mm twin-screw extruder and melt compounded at 240°C, quenched and pelletized in a continuous process. Physical properties were tested on injection molded parts, and the results recorded in Tables 21 and 22.

Table 21

Sample[1]	Component (pph		Not. Izod (ft-lbs./in)		MI @ 230°C @ 2160 g	Shore D Hardness (0 sec /15 sec)
	Modifier H[a]	Ny[b]				
NYH1	0	100	1.6[c]	1.5[d]	28	79/70
NYH2	5	95	1.9[c]	2.8[d]	26	81/71
NYH3	10	90	2.0[c]	2.9[d]	26	82/71
NYH4	20	80	2.9[c]	6.0[d]	17	79/69
NYH5	30	70	4.1[c]	13[d]	17	77/67
NYH6	40	60	NB[*]	NB	16	75/62

[1]Samples include 0.1 pph Irganox® 1010
[a]Modifier H is Sample W, hereinabove.
[b]Nylon 6 (Capron 8202).
[*]NB is "no break".
[c]Gate.
[d]Far.

Table 22

Sample	Tensile Strength @ Max/Break/Yield (psi)	Elongation @ Max/Break/Yield (%)	Flexural Modulus (psi)	Gardner Impact[1] (in.-lbs.) @ 23°C (-30°C)
NYH1	9139/6290/9125	11/160/11	171118	- (-)
NYH2	10133/10064/7948	315/316/10	166320	NB[*] (160)
NYH3	9780/9699/7777	302/310/10	170931	NB (170)
NYH4	7914/7867/5717	271/273/9	129558	NB (200)
NYH5	7721/7635/5540	262/264/9	117750	NB (172)
NYH6	6353/6335/4383	245/245/43	83500	NB (NB)

[1] 1/8" plaques, NB IS>320.
[*] NB is "no break".

In the above Examples, Initial Modulus, Tensile strength, and Elongation were determined by ASTM D-1708; Flexural Modulus was determined by ASTM D-790; Melt index was determined by ASTM D-1238; Shore A Hardness and Shore D Hardness were determined by ASTM D-2240; IZOD was determined by ASTM D-256.

CLAIMS:

1. A non-blocking chemically modified polyvinylbutyral (PVB) composition comprising a chemically modified PVB, wherein the modified PVB is the reaction product of unmodified polyvinylbutyral, having hydroxyl functionality, and a second component or mixture, wherein the second component reacts with at least a portion of the hydroxyl functionality of the PVB.

2. The PVB composition of Claim 1, wherein the PVB composition does not block at a temperature in the range of from above about 4°C to below about 75°C.

3. The PVB composition of Claim 2 wherein the PVB composition does not block at a temperature in the range of from above about 4°C to below about 60°C.

4. The PVB composition of Claim 3 wherein the PVB composition does not block at a temperature in the range of from above about 4°C to below about 50°C.

5. The PVB composition of Claim 1 wherein the second component is a polymer having functional groups selected from the group consisting of: anhydrides, carboxylic acids, carboxylic acid esters, or mixtures of any of these.

6. The composition of any of Claims 1 – 5 wherein the pellets include at least one other thermoplastic polymer selected from the group consisting of: polyvinylchloride; nylon; polypropylene; polyethylene; olefinic copolymers; like polymers or mixtures thereof.

7. A process for converting polyvinylbutyral into pellet form, wherein the pellets do not adhere to one another in such a manner that they become blocked, the process comprising the steps: (i) mixing polyvinylbutyral and a second component or mixture under conditions suitable to cause a reaction between PVB and at least one other component to obtain a chemically modified PVB composition, wherein the other component is reactive with hydroxyl functionality; and (ii) converting the

modified PVB composition into pellet form by physical or mechanical means at a temperature of above about 4°C.

8. The process of Claim 7 wherein the pellets are obtained by a continuous process.

9. A continuous process for obtaining blends of modified PVB with a thermoplastic polymer comprising the step: continuously mixing a modified PVB composition with a thermoplastic polymer composition.

10. The process of Claim 9 wherein the thermoplastic polymer is selected from the group consisting of: polypropylene; polyvinyl chloride; nylon, and olefinic copolymers.

11. An article comprising the composition of either of Claims 1 or 6.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 February 2002 (14.02.2002)

PCT

(10) International Publication Number
WO 02/12356 A3

(51) International Patent Classification[7]: C08F 8/14, C08G 81/02, C08L 29/14

(21) International Application Number: PCT/US01/25283

(22) International Filing Date: 10 August 2001 (10.08.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/224,126 10 August 2000 (10.08.2000) US

(71) Applicant *(for all designated States except US)*: **E.I. DUPONT DE NEMOURS AND COMPANY** [US/US]: 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **HOFMANN, George, Henry** [US/US]: 102 Weldin Park Drive, Wilmington, DE 19803 (US).

(74) Agent: **DOBSON, Kevin, S.**: E.I. Dupont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
-- *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

(88) Date of publication of the international search report:
2 May 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/12356 A3

(54) Title: PROCESS FOR CONVERSION OF POLYVINYL BUTYRAL (PVB) SCRAP INTO PROCESSABLE PELLETS

(57) Abstract: The present invention relates to a polyvinylbutyral (PVB) composition that is useful for blending with other polymers. The PVB composition of the present invention can be stored and used at ambient temperature without the occurrence of blocking by the PVB.

INTERNATIONAL SEARCH REPORT

Interr nal Application No
PCT/US 01/25283

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F8/14 C08G81/02 C08L29/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F C08G C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 853 097 A (ARMSTRONG WORLD INDUSTRIES, INC.) 15 July 1998 (1998-07-15) column 1, line 41 - line 57 column 2, line 58 -column 3, line 46; claims 1-20	1-6
Y	WO 93 02141 A (DU PONT DE NEMOURS AND COMPANY) 4 February 1993 (1993-02-04) page 2, line 29 -page 3, line 24 page 4, line 33 -page 6, line 36 page 7, line 11 -page 8, line 30; claims 1-8	1-11
Y	US 5 770 654 A (P. S. BLATZ) 23 June 1998 (1998-06-23) cited in the application column 3, line 31 - line 43; claims 1-16	1-11

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 March 2002	18/03/2002
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Permentier, W

1

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 434 915 A (W. E. GARRISON) 25 March 1969 (1969-03-25) column 3, line 41 -column 4, line 16; claims 1-12	1-11
Y	EP 0 834 520 A (CLARIANT GMBH) 8 April 1998 (1998-04-08) column 2, line 46 -column 3, line 10; claims 1-13	1-11
A	US 3 736 311 A (P. M. SUBRAMANIAN) 29 May 1973 (1973-05-29) claims 1-6	1
A	EP 0 778 292 A (BAYER CORPORATION) 11 June 1997 (1997-06-11) page 3, line 22 -page 4, line 43; claims 1-21	1
A	US 2 533 314 A (F. GROFF) 12 December 1950 (1950-12-12) the whole document	1
A	US 2 828 289 A (J. W. MENCH) 25 March 1958 (1958-03-25) the whole document	1

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 01/25283

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 853097	A	15-07-1998	EP	0853097 A1	15-07-1998
			GB	2321059 A	15-07-1998
			NO	980120 A	14-07-1998
WO 9302141	A	04-02-1993	MX	9204288 A1	01-01-1993
			WO	9302141 A1	04-02-1993
US 5770654	A	23-06-1998	CA	2171706 A1	20-04-1995
			DE	69429453 D1	24-01-2002
			EP	0737225 A1	16-10-1996
			JP	9506377 T	24-06-1997
			JP	3217370 B2	09-10-2001
			WO	9510561 A1	20-04-1995
US 3434915	A	25-03-1969	BE	689743 A	16-05-1967
			DE	1596966 B	04-03-1971
			FR	1499848 A	27-10-1967
			GB	1093864 A	06-12-1967
			NL	6616166 A ,B	18-05-1967
EP 834520	A	08-04-1998	DE	19640731 A1	16-04-1998
			EP	0834520 A2	08-04-1998
			JP	10139812 A	26-05-1998
			TW	387918 B	21-04-2000
			US	6121349 A	19-09-2000
US 3736311	A	29-05-1973	NONE		
EP 778292	A	11-06-1997	BR	9605823 A	25-08-1998
			CA	2191946 A1	05-06-1997
			EP	0778292 A2	11-06-1997
			JP	9249712 A	22-09-1997
US 2533314	A	12-12-1950	NONE		
US 2828289	A	25-03-1958	NONE		